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(71) Applicant *(for all designated States except US)*: CENTRUM BADAŃ WYSOKOCIŚNIENIOWYCH POLSKIEJ AKADEMII NAUK [PL/PL]; ul. Sokołowska 29/37, PL–01–142 Warszawa (PL).

(71)(72) Applicants and Inventors: ŁUCNZIK, Bolesław [PL/PL]; ul. Gwiazdzista 27 m 93, PL–01–651 Warszawa (PL). SUSKI, Tadeusz [PL/PL]; ul. Lachmana 2 m 70, PL–02–786 Warszawa (PL). WRÓBLEWSKI, Mirosław [PL/PL]; ul. Nowolipie 26 m 85, PL–01–011 Warszawa (PL).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: POROWSKI, Sylwester [PL/PL]; ul. Wieniawskiego 5/7, PL–01–572 Warszawa (PL). BOCKOWSKI, Michał [PL/PL]; ul. Klaudyny, 32 m 311, PL–01–168 Warszawa (PL). GRZEGORY, Izabella [PL/PL]; ul. Nałkowskiej, 9 m 10, PL–01–886 Warszawa (PL). KRUKOWSKI, Stanisław [PL/PL]; ul. Zaranie 8, PL–02–400 Warszawa (PL). LESZCZYŃSKI, Michał [PL/PL]; ul. Meander 1[a] m 10, PL–02–791 Warszawa (PL).

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(54) Title: THE METHOD OF FABRICATION OF HIGHLY RESISTIVE GaN BULK CRYSTALS

(57) Abstract

This method according to the invention allows the fabrication of bulk GaN crystals of high specific resistivity. This is achieved by the crystallization of GaN from the solution of atomic nitrogen in molten mixture of metals, containing gallium and Periodic Table group II metals: magnesium, calcium, zinc, beryllium, cadmium, under high pressure of nitrogen, in the temperature gradient. These crystals can be used to fabrication of excellent single crystalline GaN substrates for deposition of the homoepitaxial layers and structures for the optoelectronic applications.

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The method of fabrication of highly resistive GaN bulk crystals

Field of the Invention

This Invention relates to the method of fabrication of highly resistive GaN bulk crystals for manufacturing of optoelectronic devices.

Background of the Invention

According to the present state of the art of growth of single crystals there are not known methods of manufacturing of highly resistive GaN bulk crystals.

Object and Summary of the Invention

According to the Invention, GaN crystallization is effected in the solution of atomic nitrogen in molten mixture of the metals containing gallium in the concentration not lower than 90 at % and at least one of Periodic Table group II metals: Mg, Ca, Be, Zn, Cd. in the concentration: 0.01 - 10 at % in order to reduce the concentration of free electron carriers in the crystal by change of microscopic growth mechanism leading to the improvement of the stoichiometry and compensation on nonintentionally introduced donor impurities. The process is conducted under nitrogen pressure 0.5 - 2.0 GPa and in the temperature 1300 - 1700 °C in order to assure the stability of GaN and high concentration of nitrogen in liquid solution.

Crystallization in conducted the temperature gradient not smaller than 10°C/cm, which assures low supersaturation in the growth zone, necessary to obtain GaN crystal growth velocity lower than 0.2 mm/h, necessary for stable growth of large size crystals.

In the results of the growth process hexagonal GaN plate-like crystals are obtained, having the specific resistivity 10^4 - 10^8 Ωcm, characterized by high structural quality and the lattice parameters close to the perfect crystal. These so obtained crystals, are not available at present, and can be used as perfect substrates for unstrained homoepitaxial GaN layers.

The subject of the Invention s demonstrated on the examples of applications.

Example 1

The molten mixture of semiconductor purity metals consisting of 99.5 at. % of gallium and 0.5 at. % of magnesium is poured into the vertically configured graphite crucible under the shield of inert gas. The crucible is located into the three-zone graphite furnace which is turn is positioned inside the high pressure vessel, which in the first stage is evacuated to the vacuum level of 10^{-5} Torr. The system is annealed in the vacuum in the temperature 800°C during 12 hours. After the annealing, the vessel is filled with nitrogen of 6N purity achieving the initial pressure of 10-15 MPa. Then the gas is compressed to the pressure of 1.5 GPa and after the compression, the crucible is heated to the temperature of 1550°C in such a way that the temperature along the crucible axis is kept constant. Then the temperature of the lower end of the crucible is lowered by 30°C obtaining the temperature gradient along the axis of the crucible. These conditions of the process are preserved during the period of 120 hours. After

120 of crystallization, the system is cooled down with the rate of 5°C/min to the room temperature and after that the nitrogen pressure is lowered to the atmospheric pressure. After the extraction of the crucible from the high pressure vessel, the crucible is warmed up to the temperature 50°C and the molten metal is poured out from the crucible. At the bottom of the crucible there are GaN crystals in the form of hexagonal platelets of the size of 6 - 8 mm. The GaN crystals are extracted from the crucible and etched in aqua regia in order to remove the remaining part of the metal.

GaN crystals, obtained in this process characterize by the specific resistivity equal to 10^6 Ωcm and high structural quality. The halfwidth of (0004) reflection of x-ray αCuK line is 20 - 30 arc sec, and the a and c lattice parameters are very uniform and are equal to: 3.1877 Å and 5.1848 Å, respectively.

We claim:

1. The method of fabrication of highly resistive GaN bulk crystals, characterized by crystallization from the solution of atomic nitrogen in the molten mixture of metals, containing gallium in the concentration not lower than 90 at % and the Periodic Table group II metals magnesium, calcium, zinc, beryllium, cadmium in the concentration of 0.01 - 10 at% under the nitrogen pressure 0.5 - 2.00 GPa.

2. The method of fabrication of highly resistive GaN bulk crystals according to Claim 1 characterized by the crystallization temperature 1300 - 1700°C.

3. The method of fabrication of highly resistive GaN bulk crystals, according to Claim 1 characterized by the temperature gradient not higher than 10°C/cm.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C30B9/00 C30B29/40 C30B11/00

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C30B

Documentation searched other than minimumdocumentation to the extent that such documents are included in the fields searched

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	PATENT ABSTRACTS OF JAPAN vol. 98, no. 5 & JP 10 007496 A (HITACHI CABLE LTD) see abstract	1-3
X	WO 95 04845 A (CENTRUM BADAN WYSOKOCISNIENIOWYCH) 16 February 1995 see page 11, line 3 - line 22; example 1	1-3
X	FR 2 313 976 A (LABORATOIRES D'ELECTRONIQUE ET DE PHYSIQUE APPLIQUEE LEP) 7 January 1977 see page 2, line 8 - line 9; claim 1	1-3

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[X] Further documents are listed in the continuation of box C.

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Date of the actual completion of theinternational search	Date of mailing of the international search report
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Name and mailing address of the ISA	Authorized officer
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropnate, of the relevant passages	Relevant to claim No.
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